Pyrolytic formation of monomers from hardwood lignin as studied from the reactivities of the primary products

AUTHOR(S):

Kotake, Takeo; Kawamoto, Haruo; Saka, Shiro

CITATION:

Kotake, Takeo ...[et al]. Pyrolytic formation of monomers from hardwood lignin as studied from the reactivities of the primary products. Journal of Analytical and Applied Pyrolysis 2015, 113: 57-64

ISSUE DATE:

2015-05

URL:

http://hdl.handle.net/2433/240622

Pyrolytic formation of monomers from hardwood lignin as studied from the reactivities of the primary products

Takeo Kotake, Haruo Kawamoto*, Shiro Saka

Graduate School of Energy Science, Kyoto University, Yoshida-honmachi, Sakyo-ku, Kyoto 606-8501, Japan

* Corresponding author. Tel/Fax: +81-75-753-4737. Email address: kawamoto@energy.kyoto-u.ac.jp

Abstract

The pyrolytic reactivity of sinapyl alcohol (SA), which is the expected primary product during the early stage pyrolysis of syringyl (S)-type lignin, was studied under nitrogen pyrolysis at 200–350°C for 5 min and compared with the reactivity of coniferyl alcohol (CA) from the guaiacyl (G)-type lignin. The pyrolytic pathways of SA were similar to those reported for CA, with some differences in their reactivities. The major products were the condensation products, along with smaller amounts of a variety of side-chain conversion products (*cis*-SA, sinapyl aldehyde, dihydrosinapyl alcohol, 4-propenylsyringol and 4-vinylsyringol). The recoveries of SA through its evaporation were lower than those of CA, most likely because of its low evaporation efficiency against the condensation reactivity. From the influences of the addition of an aprotic solvent (1,3-diphenoxybenzene) and a H-donor (1,2,3,10b-tetrahydrofluoranthene), SA was found to be more susceptible to the free radical reactions than CA at 350°C. This promoted secondary reactions of SA. The use of the H-donor suppressed the radical coupling reactions effectively, which led to an increase in yield of monomeric syringols. With these features in mind, monomer formation from Japanese beech (*Fagus crenata*, a hardwood) wood and milled wood lignin (MWL) was studied, as compared with those from Japanese cedar (*Cryptomeria japonica*, a softwood). Both S- and G-type monomers were obtained, which were similar to those from the SA and CA pyrolysis, respectively. The results were mostly explainable with the reactivities of SA and CA as the lignin pyrolysis intermediates, except for the differences observed between beech MWL and wood; only lignin in the beech wood produced much greater amounts of monomers than other samples at 300 and 350°C, even without addition of any H-donors for stabilization of the radical intermediates. Other wood constituents in beech, probably hemicellulose, were proposed to serve as a source of H-donors during pyrolysis.

Keywords: Pyrolysis; Molecular mechanism; Sinapyl alcohol; Hardwood lignin; Monomer formation; Role of hemicellulose.

1. Introduction

Lignin is an aromatic constituent representing approximately 20–30 wt% of wood and has chemical structures in which phenylpropane-units are linked through various ether (C-O) and condensed (C-C) type linkages. Guaiacyl (G, 4-hydroxy-3-methoxyphenyl)-, syringyl (S, 3,5-dimethoxy-4-hydroxyphenyl)- and 4-hydroxyphenyl (H)-types are known as the aromatic nuclei of lignin and their composition varies depending on the taxonomical groups of wood and other plant species. For example, softwood lignins include the G-type and a very small amount of the H-type aromatic nuclei, while hardwood lignins consist of the G- and S-type aromatic nuclei. Such differences in composition of the aromatic nuclei may affect the pyrolytic reactivities of lignins in different taxonomical groups.

Pyrolytic products from lignins have been characterized using gas chromatography mass spectroscopy and other analytical methods [1-6]. Monomeric guaiacols and syringols bearing a variety of C1 to C3 side-chains have been identified from the pyrolysis of hardwood lignins, which originated from the G- and S-type aromatic nuclei, respectively. The side-chain structures normally attached to the *p*-position of the phenolic hydroxyl groups are changed with the progress of the pyrolysis from the double bond (>C=C< and >C=O) to saturated alkyl (propyl, ethyl and methyl groups) to methyl and non-substitution (-H) types [7]. The methoxyl substituents on the aromatic nuclei are also known to change from -OCH_3 to -OH, -CH_3 and -H through two types of reactions, namely homolytic cleavage of the O-CH_3 bond and radical-induced rearrangement [8-10] Both reactions become effective at temperatures greater than 400°C [10], which are slightly higher than the temperature range (300–350°C) where lignin depolymerization typically occurs at the primary stage of pyrolysis [11-14]. These structural changes in chemical composition have been reported for both S- and G-type products. These considerations suggest that the pyrolytic pathways would be similar for these two types of lignins.

On the contrary, several papers [11-14]have reported on different features between softwood and hardwood lignin pyrolysis. For example, hardwood lignins tend to yield smaller amounts of residues after pyrolysis, which has been explained by the lower

content of condensed type linkages in hardwood lignins [11]. The C-5 carbon (a possible condensation site) of the G-type nuclei is already occupied by the methoxyl group in the S-type nuclei. Stability of these condensed type linkages against depolymerization during the primary stage of lignin pyrolysis has been confirmed by the reactivities of various types of model dimers [15,16].

The thermogravimetric analyses of hardwood lignins suggest that they are depolymerized in the lower temperature range than softwood lignins, as the maximum mass-loss rates are obtained in the lower temperature range for the S- than the G-type lignins [11-14]. Although such a difference would be attributed to the different pyrolytic reactivities of the S- and G-type lignins, to the best of our knowledge, no papers have discussed these topics. Accordingly, fundamental studies would be required for an improved understanding of the pyrolysis of the S- and G-type lignins.

For the pyrolysis of the G-type lignin, the formation of the coniferyl alcohol (CA) radical via the homolytic cleavage of the β-ether linkages, which is the most abundant of the ether linkages of lignin, followed by its secondary decomposition have been proposed as an important pathway of the G-type lignin to form condensation products and a variety of monomeric guaiacols during the primary stage of pyrolysis [17,18]. The corresponding sinapyl alcohol (SA) radical would be an important primary product from the pyrolysis of the S-type lignin. The data reported by Evans et al. [1] support this speculation. They reported that a strong signal at *m*/*z* 210 (SA) was observed together with a signal at *m*/*z* 180 (CA) in the early stage of the pyrolysis by analyzing the pyrolysis vapors from hardwood lignin using a molecular-beam mass spectrometric sampling technique.

Under these circumstances, we have studied the pyrolytic reactivities of SA from 200–350°C, in contrast with the reactivities of CA reported in our previous paper [17,18]. Using these data, the pyrolysis behaviors of Japanese beech (*Fagus crenata*) wood and its lignin fraction are discussed at the molecular level.

2. Experimental

2.1 Materials

Trans-SA (**1**) was prepared by the reduction of *trans*-sinapyl aldehyde (Sigma-Aldrich Co. LCC., St Louis, MO, USA) with sodium borohydride. 1,3-

Diphenoxybenzene (DPB, an aprotic solvent, expected boiling point: 374°C [19]) and 1,2,3,10b-tetrahydrofluoranthene (a H-donor, expected boiling point: 354°C [19]) were purchased from Tokyo Chemical Co., Ltd. (Tokyo, Japan) with guaranteed grades and used without further purification. Solvent and H-donor were selected from the candidates with higher boiling points than the temperatures applied for the pyrolysis experiments, in order to allow the interactions between samples and solvent/H-donor. The chemical structures of all compounds reported were confirmed by ^{1}H-nuclear magnetic resonance (NMR) spectra. The ^{1}H-NMR spectra were measured on a Varian AC-400 (400 MHz) spectrometer (Varian, CA, USA).

Japanese beech wood flour (< 80 mesh), which had been pre-extracted with ethanol/benzene (2:1, v/v) and the milled wood lignin (MWL) fraction isolated from the beech wood sample were used in this study. The preparation and characterization of these samples has been described previously [14,20]. The lignin content of the wood sample, which was evaluated as the total yield of Klason and acid-soluble lignins, was 23 wt%, and the S/G ratio determined by the nitrobenzene-oxidation method was 2.0 [20]. The S/V ratio of the MWL evaluated by a similar method was 2.3 [14].

2.2 Pyrolysis

The pyrolysis and fractionation of the products were described in our previous paper [17]. *Trans*-SA (5.0 mg) was placed on a Pyrex glass tube wall to a height approximately 1.5 cm from the bottom (internal diameter 8.0 mm, length 300 mm, wall thickness 1.0 mm) through evaporation from a methanol (MeOH) solution. A nitrogen bag was attached to the top of the tube reactor via a three-way tap, and the air inside the reactor was purged with nitrogen using an aspirator connected through the three-way tap. The bottom two thirds of the reactor was inserted into a muffle furnace preheated to 200–350°C, through a small hole in the top of the furnace. After heating for 5 min, the reactor was cooled immediately by flowing air over the reactor for 1 min and subsequently by cold water for 1 min.

After pyrolysis, the reactor wall was cut into two sections approximately 1.5 cm from the bottom of the reactor as shown in Fig.1. Both sections were rinsed with MeOH (1.0 mL) to recover the MeOH-soluble products together with the remaining SA. The

MeOH-soluble fractions obtained from the upper and lower parts of the reactor wall are denoted $\mathbf{F_{Upper}}$ and $\mathbf{F_{Lower}}$, respectively. Given that the SA (starting compound) was placed at the bottom of the reactor prior to heat treatment, the product recovered in the $\mathbf{F_{Upper}}$ was a volatile product that had evaporated from the bottom part of the reactor. Accordingly, we were able to analyze the volatile products (or SA) separately from those remaining in the melt/solid phase at the bottom of the reactor.

Pyrolysis of the wood or MWL samples was also conducted in a similar manner. For pyrolysis in an aprotic solvent, DPB (50 mg) was added at the bottom of the reactor. To investigate the influence of a H-donor, a mixture of DPB (50 mg) and 1,2,3,10b-tetrahydrofluoranthene (11.4 mg) was used instead of DPB.

2.3 Product analysis and quantification

Pyrolyzates obtained by repeated pyrolysis experiments (5 times) of SA were purified using preparative thin-layer chromatography (TLC) with chloroform as eluent on a silica gel plate (Kieselgel 60 F_{254}, Merck). Three major fractions, A, B and C, with R_f values of 0.47, 0.24 and 0.07, respectively, were obtained. By comparison of the ^{1}H-NMR spectra of these fractions with those obtained from the pyrolysis of CA, it was found that the fractions A, B and C included 4-propenylsyringol (**5**) and 4-vinylsyringol (**6**), sinapyl aldehyde (**3**) and *trans*- (**1**) and *cis*- (**2**) isomers of SA, respectively, as the major compounds. Further purification of each fraction on TLC enabled us to isolate products **2**–**6**, which were completely identified with their ^{1}H-NMR spectra.

A quantification of these products and the recovered SA was conducted by analyzing the MeOH-soluble portions by high-performance liquid chromatography (HPLC) on a Shimadzu LC-10A system (Shimadzu, Kyoto, Japan) using a Cadenza CD C-18 column with flow rate of 0.7 mL/min at 40°C. A binary solvent system composed of MeOH and H_2O was used for the HPLC analysis with a gradient of 30/70 (0 min) → 45/55 (0 min → 5 min), 45/55 (5 min → 25 min) → 100/0 (25 min → 55 min) and 100/0 (55 min → 70 min). The HPLC system was equipped with an ultraviolet (UV) detector operating at 280 nm. The product yields and recoveries of SA were determined from a comparison of their peak areas with that of 1,2,3-trimethoxybenzene, which was used as an internal standard.

Gel-permeation chromatography (GPC) was used to obtain molecular weight (MW) distribution information for the MeOH-soluble products using the Shimadzu LC-10A system with a Shodex KF-801 column (exclusion limit: 1,500, polystyrene standard) at a flow rate of 0.6 mL/min and 40°C. Tetrahydrofuran was used as eluent with UV detection at 280 nm.

3. Results and discussion

3.1 Reactivity: sinapyl alcohol vs coniferyl alcohol

SA was pyrolyzed under nitrogen at 200–350°C for 5 min and the pyrolyzates were recovered in two fractions, that is, $\mathbf{F_{Upper}}$ and $\mathbf{F_{Lower}}$. Fig 2 illustrates results of the GPC analyses of the $\mathbf{F_{Upper}}$ and $\mathbf{F_{Lower}}$ fractions. The enlarged chromatograms also include data of the pyrolysis of CA conducted at 300 and 350°C [17]. The signals at 13 min, which correspond to SA, started to decrease at 250°C and disappeared completely at 300°C in the $\mathbf{F_{Lower}}$ fractions. The intensities of the signals (SA) in the $\mathbf{F_{Upper}}$ fractions were comparatively smaller at all temperatures. These observations indicate that the evaporation of SA was not effective in this temperature range. These features were similar to those reported for CA [17]. The evaporation behavior is shown quantitatively in Fig. 3, as compared with the data of CA [17]. The recoveries of SA from the $\mathbf{F_{Upper}}$ fractions were only 0.6, 3.1, 3.3 and 2.5 % at 200, 250, 300 and 350°C, respectively and these values were much smaller than those obtained for CA. Thus, SA is more difficult to evaporate from the heating zone than CA, if formed during lignin pyrolysis. The higher estimated boiling point of SA (385°C [19]) than that of CA (332°C [19]), which is attributed to the additional methoxyl group, would be a reason for the lower SA volatility.

As observed in the pyrolysis of CA, the condensation reaction occurred preferentially for SA (Figs. 2 and 3). The GPC data (enlarged chromatograms) in Fig. 2 indicate that CA yielded condensation products with higher molecular masses than SA. This would be attributed to the C-5 carbon of the G-nucleus of CA, which is a potential site for condensation in the mechanisms via the quinone methide intermediate as proposed in literature [17,21]. It should be noted that the condensation reaction of SA proceeded, even though the C-5 carbon is already occupied by a methoxyl group. The side-chain C_β and aromatic C-2 and C-6 carbons would be involved in the condensation

reactions, although further study is necessary for a complete understanding of the condensation reactions of SA.

The signals observed at the longer retention times than those of SA in the $\mathbf{F_{Upper}}$ fractions (Fig. 2) suggest the formation of low MW products from SA, which were evaporated from the bottom. As shown in an example of the HPLC data (350°C, $\mathbf{F_{Upper}}$ fraction) (Fig. 4), syringol derivatives with a variety of side-chains at the *p*-positions to the phenolic hydroxyl groups were identified, which included *cis*-SA (**2**), sinapyl aldehyde (**3**, an oxidation product), dihydrosinapyl alcohol (**4**) and 4-propenylsyringol (**5**) (reduction products) and 4-vinylsyringol (**6**) with a C2 side-chain. These products had the same types of side-chains observed in the corresponding guaiacols obtained from the pyrolysis of CA. Thus, the same type of side-chain conversion reactions took place during SA and CA pyrolysis. The formation mechanisms have been discussed in detail in our previous paper [17] and include the free radical and quinone methide pathways.

The yields of monomeric syringols in the $\mathbf{F_{Upper}}$ and $\mathbf{F_{Lower}}$ fractions are summarized in Fig. 5, as compared with those (total yields) of the corresponding guaiacol derivatives obtained from the pyrolysis of CA [17]. As observed in the pyrolysis of CA, these products tended to be recovered from the $\mathbf{F_{Lower}}$ fractions at lower temperatures, while the yields from the $\mathbf{F_{Upper}}$ fractions increased gradually with an increase in pyrolysis temperature. These observations suggest that the side-chain conversion products were formed in the liquid phase and then evaporated at higher temperatures. Although the boiling points of the S-type derivatives are expected to be higher than those of the corresponding G-types due to additional methoxyl group, their yields were not very different from those from CA, except for 4-vinylsyringol (**6**). The yields of compound **6** were much lower than those of 4-vinylguaiacol from CA at all temperatures studied.

The polymerization reaction of CA has been reported to be suppressed effectively in aprotic solvents such as DPB [18]. Accordingly, the recoveries of SA (from $\mathbf{F_{Upper}}$ + $\mathbf{F_{Lower}}$) during SA pyrolysis between the neat and solution (in DPB) conditions were compared. The results are illustrated in Fig. 6, together with the CA data [17]. At 250 and 300°C, pyrolysis in DPB effectively inhibited the polymerization to increase the SA recovery and the situation was very similar to that of CA. An inhibition mechanism in DPB has been proposed in our previous paper [18]; the proton-transfer, which is required

for the heterolytic formation of the quinone methide intermediates for condensation, is suppressed effectively in DPB by solvation to CA. In contrast, at 350°C, unlike the pyrolysis of CA, the recovery of SA dropped significantly even in DPB. Furthermore, additional pyrolysis experiments using a mixture of SA and CA (1:1, w/w) revealed that even the decomposition of CA was accelerated in the presence of SA. These results indicate that the free radical reactions of SA would prevail at 350°C, which accelerates the decomposition of CA in the mixture pyrolysis. To confirm this point, the influence of a H-donor (1,2,3,10b-tetrahydrofluoranthene) addition was investigated for SA pyrolysis at 350°C.

The recoveries of SA and yields of side-chain conversion products after SA pyrolysis in DPB in the presence of the H-donor at 350°C are summarized in Fig. 7, compared with data under the neat and solution (in DPB) conditions. The data obtained for CA [18] are also shown for comparison. Although the total monomer yields including CA were not altered significantly by addition of the H-donor in CA pyrolysis in DPB, the use of the H-donor increased these values significantly in the case of SA.

As observed in the pyrolysis of CA [18], the addition of the H-donor promoted the side-chain reduction to enhance the formation of dihydrosinapyl alcohol (**4**) and 4-propenylsyringol (**5**), probably through the addition of the hydrogen radical, which is formed through decomposition of the H-donor, to the double bonds. Thus, in CA pyrolysis, yields of side-chain reduction products and recovery of CA are in a trade-off relationship. On the other hand, yields of all monomers including SA increased by the addition of the H-donor to the SA solution in DPB. These results confirm the proposal that the free radical reactions prevail during the pyrolysis of SA at 350°C, which leads to the formation of the coupling products. These radical coupling reactions would be effectively inhibited by the H-donor and the hydrogen radicals formed through decomposition of the H-donor.

Based on the results, some features were identified for the pyrolytic reactivities of SA and CA. Large part of the SA was converted to the polymerization products before its evaporation, and this tendency was greater than CA. SA was more susceptible to the free radical reactions than CA at 350°C, and this led to the reduction of the monomer yield through formation of the radical coupling products.

3.2 Formation of monomers from pyrolysis of hardwood lignin

With the features of SA and CA in mind, the pyrolysis of Japanese beech wood and the MWL fraction were studied under pyrolysis conditions (nitrogen/250–350°C/5 min). Influences of solvent (DPB) and H-donor (1,2,3,10b-tetrahydrofluoranthene) were also investigated. The results were compared with those of Japanese cedar (*Cryptomeria japonica*), a softwood, reported in our previous paper [18]).

The yields of monomeric products from the pyrolysis of Japanese beech wood and MWL are summarized in Table 1, and changes in the compositions (wt%) of the product guaiacols and syringols depending on the pyrolysis condition are illustrated in Fig. 8. The total yields of the guaiacol- and syringol-type monomers are also shown in Fig. 9, as compared with those of the guaiacol-type monomers obtained from the pyrolysis of cedar wood and MWL [18]. Dihydroconiferyl alcohol from the beech wood/MWL could not be determined because of peak overlapping during HPLC analysis.

Both guaiacols and syringols were obtained from the pyrolysis of the beech wood and MWL, and the HPLC chromatograms were quite similar to the summative one of the pyrolysis of CA and SA. These results support the hypothesis; CA and SA are the important primary products from the early stage pyrolysis of hardwood lignins, although CA and SA were not obtained as the dominant products. Any SA was not detected in pyrolysis of the beech MWL and wood under the neat conditions, except for the condition of beech wood/350°C, and the proportion of CA in the monomeric guaiacols was only less than 13 wt% under the neat conditions (Table 1, Fig. 8). Secondary decompositions discussed earlier would occur to reduce the yields of CA and SA. The “polymer” effect was suggested in our previous paper [18] to explain the more prevailing secondary reactions during pyrolysis of cedar lignins than expected from the results of CA pyrolysis; monomeric products are stabilized through evaporation from the heating zone, but the pyrolytic cleavage of one of the ether linkages in the lignin polymer chains does not form the volatile monomers immediately; consequently, the primary structures with more labile conjugated double bonds formed in the polymer chain ends would tend to be subject to the secondary reactions including side-chain conversions and condensation, before monomer formation. Formation of the primary products as radical

species, which arise from the homolytic cleavage of lignin ether linkages [22], also promotes the secondary reactions.

Pyrolysis in DPB improved the yields of CA and SA from both wood and MWL samples (Table 1), and hence, these proportions increased in DPB up to around 50% at 250°C (Fig. 8). These results are explainable with the inhibitory effect of DPB for polymerization of CA and SA, as described earlier.

Pyrolysis temperature is an important factor for the monomer yield and the monomer composition. Since maximum mass-loss rates have been observed around 330–360°C in the thermogravimetric analysis of softwood and hardwood lignins [11-14], the monomer yield tend to increase with an increase in pyrolysis temperature from 250 → 300 → 350°C (Fig. 9), except for the condition of beech MWL/in DPB/350°C, where the monomer yield was rather lower than that obtained at a lower pyrolysis temperature of 300°C. This is explainable with the earlier conclusion; SA is more susceptible to the free radical reactions to form the condensation products even in DPB at 350°C (Fig. 7), which would reduce the monomer yields from the beech MWL. No such effects were observed in pyrolysis of the beech wood. This is discussed later in terms of the role of H-donor during pyrolysis.

The monomer composition also changed significantly depending on the pyrolysis temperature. Generally, sinapyl aldehyde and coniferyl aldehyde (oxidation products) were formed more selectively at a low pyrolysis temperature of 250°C (Fig. 8). By increasing the pyrolysis temperature from 250 to 350°C, the compositions changed to those including more side-chain reduction products (dihydro SA, 4-propenylsyringol and isoeugenol). These influences of the pyrolysis temperature would arise from the different pyrolysis environment conditions, which would change from more radical (250°C) to more H-donor (350°C) conditions, as indicated by Kotake et al [18]. Sinapyl aldehyde and coniferyl aldehyde could form via the hydrogen abstraction reactions from the C_{γ}-hydrogens of SA and CA by the radical species formed through the homolytic cleavage of the lignin ether linkages [17].

At relatively high temperatures of 300 and 350°C, the yields of monomers from the beech wood were greater than those from the MWL, even without addition of any H-donor. Such remarkable differences have not been observed for pyrolysis of cedar wood

and MWL in our earlier paper [18]. Accordingly, this would be a characteristic feature of hardwood pyrolysis. Kotake et al. [18] have pointed out that the use of H-donor is quite important to increase the yields of monomers from pyrolysis of softwood lignins. H-Donor stabilizes the radical intermediates, which are formed through homolytic cleavage of lignin ether linkages, against the radical coupling reactions. Thus, the addition of H-donor significantly increased the monomer yield from the beech MWL and the cedar MWL and wood at 350°C (Fig. 9). It should be noted that the influence of the H-donor addition to the beech wood pyrolysis was comparatively small. These lines of evidence suggest the following hypothesis; H-donors and hydrogen radicals are supplied to the pyrolysis environment during the beech wood pyrolysis, which stabilize the radical intermediates, as illustrated in Fig. 10.

Lignin is known to coexist with hemicellulose in an amorphous matrix, which surrounds cellulose crystallites in wood cell wall. The chemical composition of hemicellulose varies depending on the taxonomic groups of wood species, i.e., softwood and hardwood. Furthermore, hemicellulose decomposes in the temperature range of 250–300°C, which is overlapped with the temperatures at which the primary pyrolysis of lignin occurs. These observations led to the hypothesis; thermal decomposition of hemicellulose in the beech wood is a source of H-donor, although further study is necessary to confirm the hypothesis.

Conclusions

(1) Analogous to CA, SA yielded condensation products preferentially.
(2) The recoveries of SA through its evaporation were lower than those of CA, most likely because of its low evaporation efficiency against the condensation reactivity.
(3) Similar types of side-chain-conversion reactions occurred for both SA and CA. The yields of 4-vinylsyringol tended to be lower than those of 4-vinylguaiacol from CA pyrolysis.
(4) Use of an aprotic solvent (DPB) increased the recoveries of SA at 250 and 300°C through suppression of the condensation reactivity. Unlike for CA pyrolysis, DPB was insufficient to increase recovery at 350°C. The additional use of a H-donor was

required to increase the monomeric syringol recoveries, including SA. Based on these results, it has been suggested that SA is more susceptible to the free radical reactions than CA at 350°C.

(5) The formation behavior of monomeric guaiacols and syringols from the pyrolysis of Japanese beech wood and MWL were explained by the reactivities of CA and SA as the pyrolysis intermediates formed as radical species through homolytic cleavage of lignin ether linkages during pyrolysis.

(6) The addition of a H-donor significantly increased the monomer yield from Japanese beech MWL as reported for Japanese cedar (a softwood) wood and MWL, while the influence was much smaller for pyrolysis of Japanese beech wood. Even without the addition of a H-donor, the wood sample gave monomers in much higher yields at 300 and 350°C. These features were suggested to be characteristic of hardwood species.

(7) A hypothesis has been proposed, in which the pyrolysis of other wood constituents (probably hemicellulose) of beech wood acts as a source of H-donors and H-radicals for stabilizing intermediate radicals.

Acknowledgments

This work was supported by a Grant-in-Aid for Scientific Research (B)(2) (No. 24380095, 2012.4-2016.3) and the Kyoto University Global COE program for “Energy Science in the Age of Global Warming” from Ministry of Education, Culture, Sports, Science and Technology, Japan.

References

[1] R.J. Evans, T.A. Milne, Molecular characterization of the pyrolysis of biomass 1. Fundamentals, Energy Fuels 1 (1987) 123-137.

[2] W. Genuit, J.J. Boon, O. Faix, Characterization of beech milled wood lignin by pyrolysis-gas chromatography-photoionization mass spectrometry, Anal. Chem. 59 (1987) 508-513.

[3] J. Ralph, R.D. Hatfield, Pyrolysis-GC-MS characterization of forage materials. J. Agric. Food Chem. 39 (1991) 1426-1437.

[4] K. Sipilä, E. Kuoppala, L. Fagernäs, A. Oasmaa, Characterization of biomass-based flash pyrolysis oils, Biomass Bioenergy 14 (1998) 103-113.

[5] B. Scholze, D. Meier, Characterization of the water-insoluble fraction from pyrolysis oil (pyrolytic lignin). Part I. PY-GC-MS, FTIR, and functional groups, J. Anal. Appl. Pyrolysis 60 (2001) 41-54.

[6] M.E. Arias, O. Polvillo, J. Rodríguez, M. Hernández, J.A. González-Pérez, F.J. González-Vila, Thermal transformations of pine wood components under pyrolysis/gas chromatography/mass spectrometry conditions, J. Anal. Appl. Pyrolysis 77 (2006) 63-67.

[7] T. Hosoya, H. Kawamoto, S. Saka, Secondary reactions of lignin-derived primary tar components, J. Anal. Appl. Pyrolysis 83 (2008) 78-87.

[8] A. Vuori, Pyrolysis studies of some simple coal related aromatic methyl ethers, Fuel 65 (1986) 1575-1583.

[9] E. Dorrestijn, P. Mulder, The radical-induced decomposition of 2-methoxyphenol, J. Chem. Soc., Perkin Trans. 2 (1999) 777-780.

[10] M. Asmadi, H. Kawamoto, S. Saka, Thermal reactions of guaiacol and syringol as lignin model aromatic nuclei, J. Anal. Appl. Pyrolysis 92 (2011) 88-98.

[11] D.J. Gardner, T.P. Schultz, G.D. McGinnis, The pyrolytic behavior of selected lignin preparations, J. Wood Chem. Technol. 5 (1985) 85-110.

[12] O. Faix, E. Jakab, F. Till, T. Székely, Study on low mass thermal-degradation products of milled wood lignins by thermogravimetry-mass-spectrometry, Wood Sci. Technol. 22 (1988) 323-334.

[13] E. Jakab, O. Faix, F. Till, Thermal decomposition of milled wood lignins studied by thermogravimetry/mass spectrometry, J. Anal. Appl. Pyrolysis 40-41 (1997) 171-186.

[14] M. Asmadi, H. Kawamoto, S. Saka, Gas- and solid/liquid-phase reactions during pyrolysis of softwood and hardwood lignins, J. Anal. Appl. Pyrolysis 92 (2011) 417-425.

[15] H. Kawamoto, S. Horigoshi, S. Saka, Pyrolysis reactions of various lignin model dimers, J.Wood.Sci. 53 (2007) 168-174.

[16] T. Nakamura, H. Kawamoto, S. Saka, Pyrolysis behavior of Japanese cedar wood lignin studied with various model dimers, J. Anal. Appl. Pyrolysis 81 (2008) 173-182.

[17] T. Kotake, H. Kawamooto, S. Saka, Pyrolysis reactions of coniferyl alcohol as a model of the primary structure formed during lignin pyrolysis, J. Anal. Appl. Pyrolysis 104 (2013) 573-584.

[18] T. Kotake, H. Kawamooto, S. Saka, Mechanisms for the formation of monomers and oligomers during the pyrolysis of a softwood lignin, J. Anal. Appl. Pyrolysis 105 (2014) 309-316.

[19] Scifinder, Chemical Abstracts Service: Columbus, OH; https://scifinder.cas.org (accessed July 24, 2014); calculated using Advanced Chemistry Devepolement (ACD/Labs) Software V11.02.1994-2013.

[20] R. Harifara, S. Ayada, S. Saka, Quantitative method applicable for various biomass species to determine their chemical composition, Biomass Bioenergy 35 (2011) 4630-4635.

[21] T. Nakamura, H. Kawamoto, S. Saka, Condensation reactions of some lignin related compounds at relatively low pyrolysis temperature, J. Wood Chem. Technol. 27 (2007) 121-133.

[22] H. Kawamoto, T. Nakamura, S. Saka, Pyrolytic cleavage mechanisms of lignin-ether linkages: A study on *p*-substituted dimers and trimers, Holzforschung 62 (2008) 50-56.

Table 1

		Guaiacols						Syringols						Total G	Total S	Total
		CA (*trans*)	CA (*cis*)	Dihyd CA	Iso EU	CAld	VG	SA (*trans*)	SA (*cis*)	Dihyd SA	PS	SAld	VS			
Beech MWL																
Neat	250°C	0.01	0	-*	0.01	0.08	0.01	0	0	0	0	0.08	0	0.11	0.08	0.19
	300°C	0.06	0.02	-	0.20	0.19	0.14	0	0	0	0.06	0.29	0.07	0.61	0.42	1.03
	350°C	0.07	0.04	-	0.30	0.15	0.27	0	0	0	0.09	0.27	0.15	0.83	0.50	1.33
In DPB	250°C	0.11	0.02	-	0.03	0.20	0.05	0.11	0.02	0	0.02	0.42	0.05	0.41	0.61	1.02
	300°C	0.04	0.03	-	0.37	0.25	0.16	0.06	0.05	0	0.17	0.68	0.12	0.84	1.08	1.92
	350°C	0.14	0.02	-	0.24	0.06	0.13	0.09	0.04	0.38	0.12	0.20	0.13	0.59	0.97	1.56
In DPB + H-donor	350°C	0.07	0.07	-	2.82	0.17	0.33	0.08	0	0.52	1.96	0.45	0.37	3.47	3.36	6.83
Beech wood																
Neat	250°C	0.02	0	-	0	0.20	0	0	0	0	0	0.18	0	0.22	0.18	0.40
	300°C	0.04	0.03	-	0.50	0.35	0.33	0	0	0.85	0.31	0.84	0.42	1.25	2.42	3.67
	350°C	0.07	0.05	-	1.01	0.32	0.75	0.12	0	2.19	0.68	0.93	0.96	2.19	4.87	7.06
In DPB	250°C	0.13	0	-	0	0.11	0	0.11	0	0	0	0.12	0	0.23	0.23	0.47
	300°C	0.34	0.05	-	0.38	0.31	0.15	0.86	0.17	0	0.26	1.04	0.23	1.24	2.56	3.79
	350°C	0.33	0.12	-	1.94	0.41	1.07	0.36	0.21	2.52	1.60	1.27	1.85	3.86	7.81	11.66
In DPB + H-donor	350°C	0.44	0.11	-	4.13	0.34	0.64	0.53	0.24	4.04	3.89	1.12	1.00	5.66	10.82	16.48

CA: coniferyl alcohol, Dihyd CA: dihydroconiferyl alcohol, Iso EU: isoeugenol, CAld: coniferyl aldehyde, VG: 4-vinylguaiacol, SA: sinapyl alcohol, Dihyd SA: dihydrosinapyl alcohol, PS: 4-propenylsyringol, SAld: sinapyl aldehyde, VS: 4-vinylsyringol.
* not determined

Legends of figure and table

Fig. 1 Reactor following the pyrolysis of sinapyl alcohol (N_2/300°C/5min) and two fractions obtained by the cutting of the reactor and subsequent extraction with methanol.

Fig. 2 Gel permeation chromatograms of methanol-soluble portions obtained by pyrolysis of sinapyl alcohol (SA) at various temperatures (N_2/5 min), compared with pyrolysis of coniferyl alcohol (CA) [17].

a: retention time of SA

−·−·−: 200°C, −−−−: 250°C, ------: 300°C, ——: 350°C

Fig. 3 Recoveries of sinapyl alcohol (SA) from $\mathbf{F_{Upper}}$ and $\mathbf{F_{Lower}}$ fractions after pyrolysis of SA at various temperatures (N_2/5 min), compared with pyrolysis of coniferyl alcohol (CA) [17].

○ : $\mathbf{F_{upper}}$, △ : $\mathbf{F_{Lower}}$, —— : SA, −−−− : CA

Fig. 4 HPLC chromatogram of methanol-soluble portion ($\mathbf{F_{Upper}}$) obtained by pyrolysis of sinapyl alcohol (N_2/350°C/5 min) with identification of certain signals.

IS (internal standard): 1,2,3-trimethoxybenzene

Fig. 5 Monomeric syringol yields from pyrolysis of sinapyl alcohol (N_2/200–350°C/5 min).

■ : $\mathbf{F_{Lower}}$, ⊡ : $\mathbf{F_{Upper}}$, ○ : total

X : yields ($\mathbf{F_{Lower}}$ + $\mathbf{F_{Upper}}$) of corresponding monomeric guaiacols obtained from pyrolysis of coniferyl alcohol under similar pyrolysis conditions [17].

Fig. 6 Influence of addition of aprotic solvent (1,3-diphenoxybenzene, DPB) on sinapyl alcohol (SA) and coniferyl alcohol (CA) recovery during pyrolysis (N_2/250–350°C/5 min).

○ : neat condition, △ : in DPE (1,3-diphenoxybenzene), ——— : SA,

– – – – : CA [18], –·–·– : recovery of CA from pyrolysis of a CA+SA mixture (1:1, w/w)

Fig. 7 Influence of addition of aprotic solvent (1,3-diphenoxybenzene, DPB) and H-donor (1,2,3,10b-tetrahydrofluoranthene) on sinapyl alcohol (SA) and coniferyl alcohol (CA) recoveries and yields of monomeric products during SA and CA [18] pyrolysis (N_2/350°C/5 min).

* H-donor/SA or CA = 11.4 mg/5.0 mg

Products from SA: 4-substituted syringols, products from CA: 4-substituted guaiacols

Substituent:

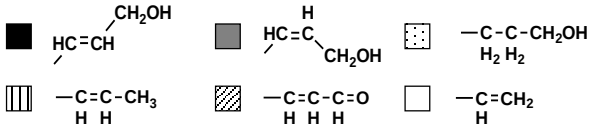
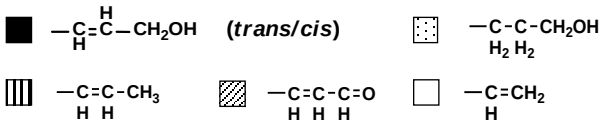


Fig. 8 Influence of pyrolysis temperature on monomeric guaiacol (G) and syringol (S) compositions obtained from pyrolysis of Japanese beech MWL and wood under neat conditions (A) and in DPB (B).

H-donor/wood or MWL = 11.4 mg/5.0 mg

Products: 4-substituted syringols and 4-substituted guaiacols

Substituent:



Dihydroconiferyl alcohol from Japanese beech wood and MWL could not be quantified because of peak overlapping during HPLC analysis.

Fig. 9 Influence of addition of aprotic solvent (1,3-diphenoxybenzene, DPB) and H-donor (1,2,3,10b-tetrahydrofluoranthene) on monomeric product yields from pyrolysis of Japanese beech wood and MWL (N_2/250–350°C/5 min).

*[1] Dihydroconiferyl alcohol from Japanese beech wood and MWL could not be quantified because of peak overlapping during HPLC analysis.

*[2] H-donor/lignin or wood = 11.4 mg/5.0 mg

□ : syringols, ■ : guaiacols

---●--- : total yields of monomeric guaiacols obtained from pyrolysis of Japanese cedar wood and MWL [18].

Fig. 10 Expected role of H-donor/H-radical in the formation of monomeric products from lignin during pyrolysis of Japanese beech wood.

Table 1 Yields (wt%, lignin-basis) of monomeric guaiacols and syringols from pyrolysis of Japanese beech MWL and wood under various pyrolysis conditions.

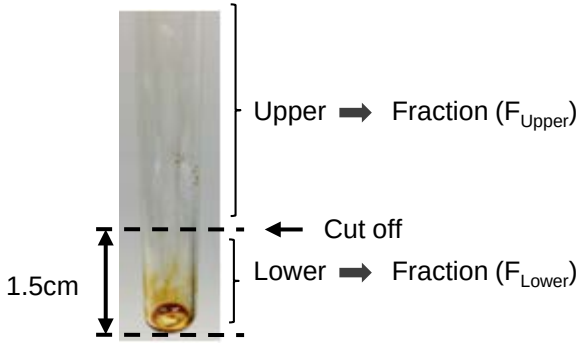


Fig. 1 (single column)

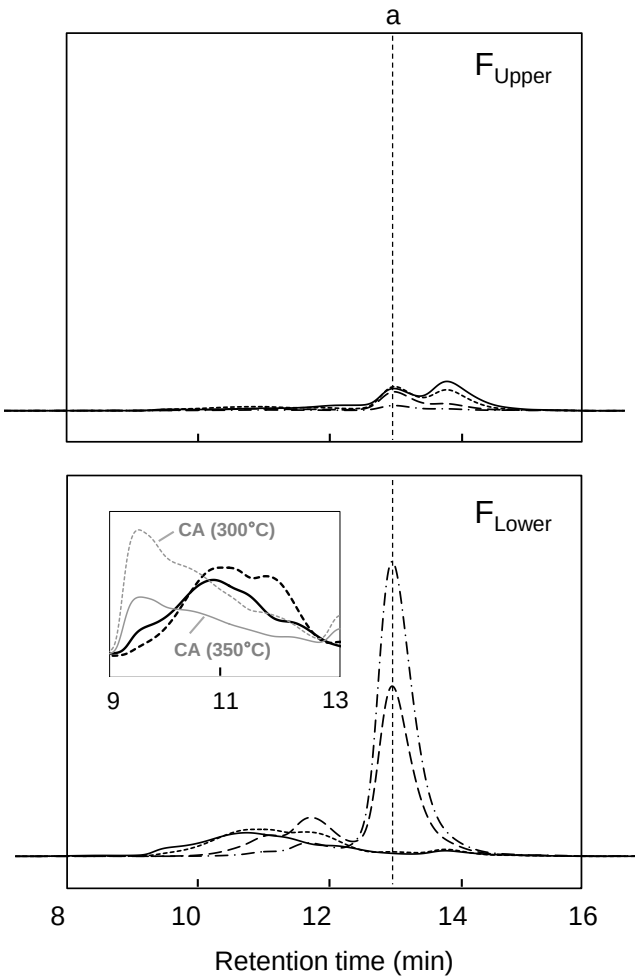


Fig. 2 (single column)

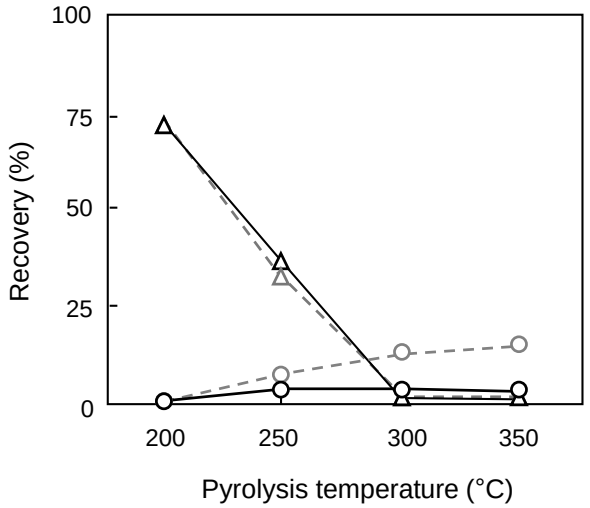


Fig. 3 (single column)

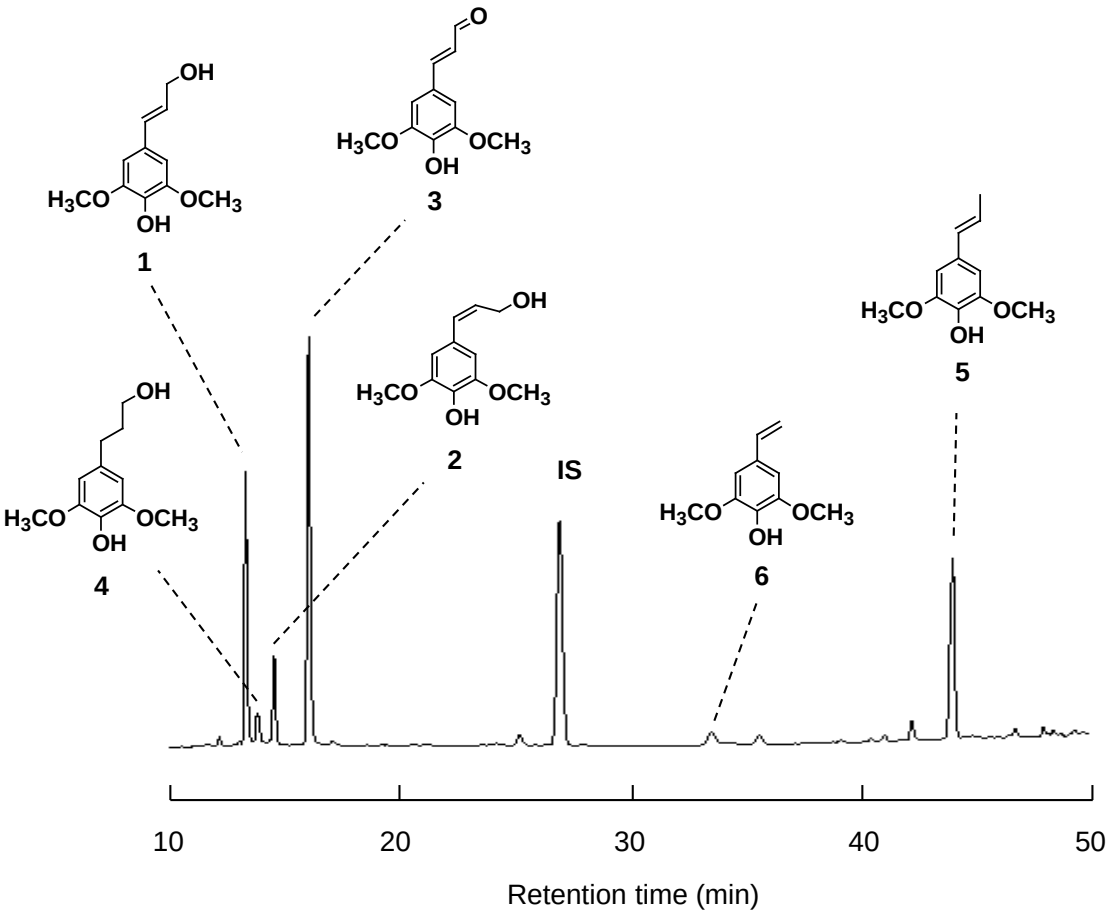


Fig. 4 (single column or 1.5 column)

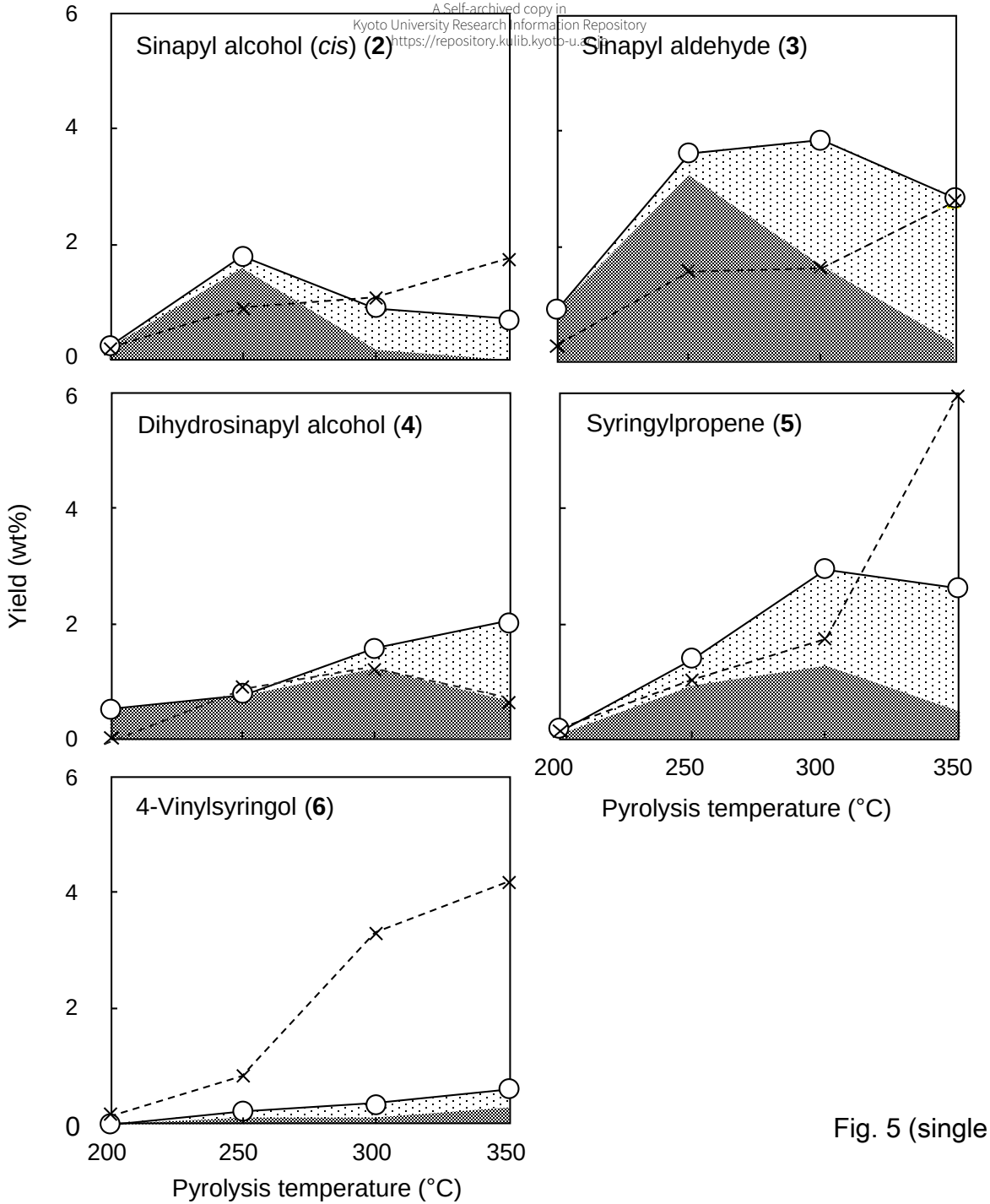


Fig. 5 (single column)

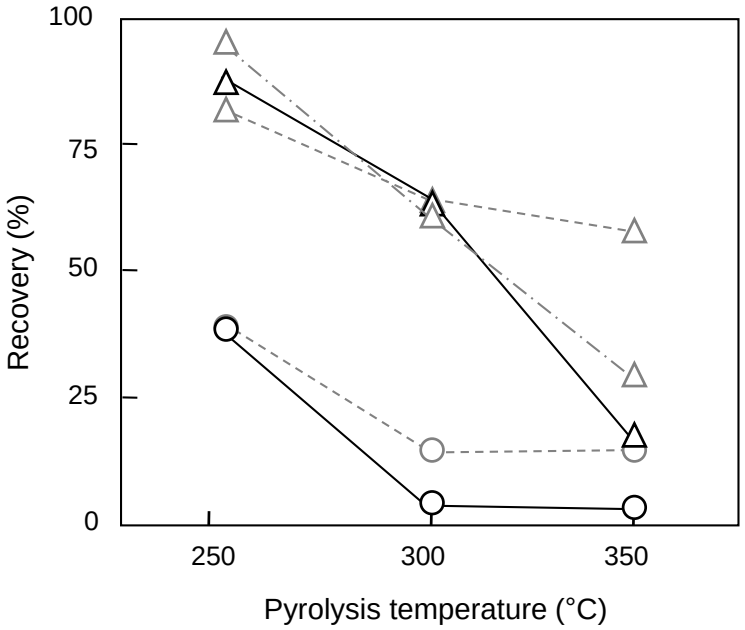


Fig.6 (single column)

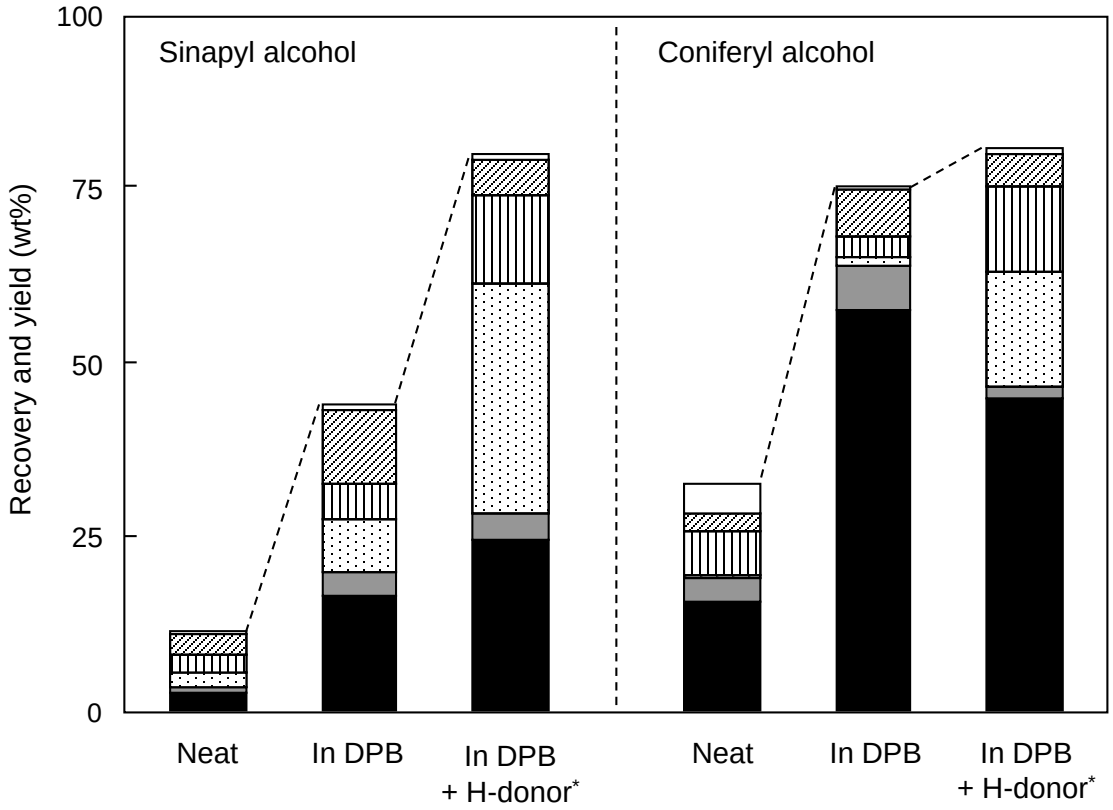


Fig.7 (single column)

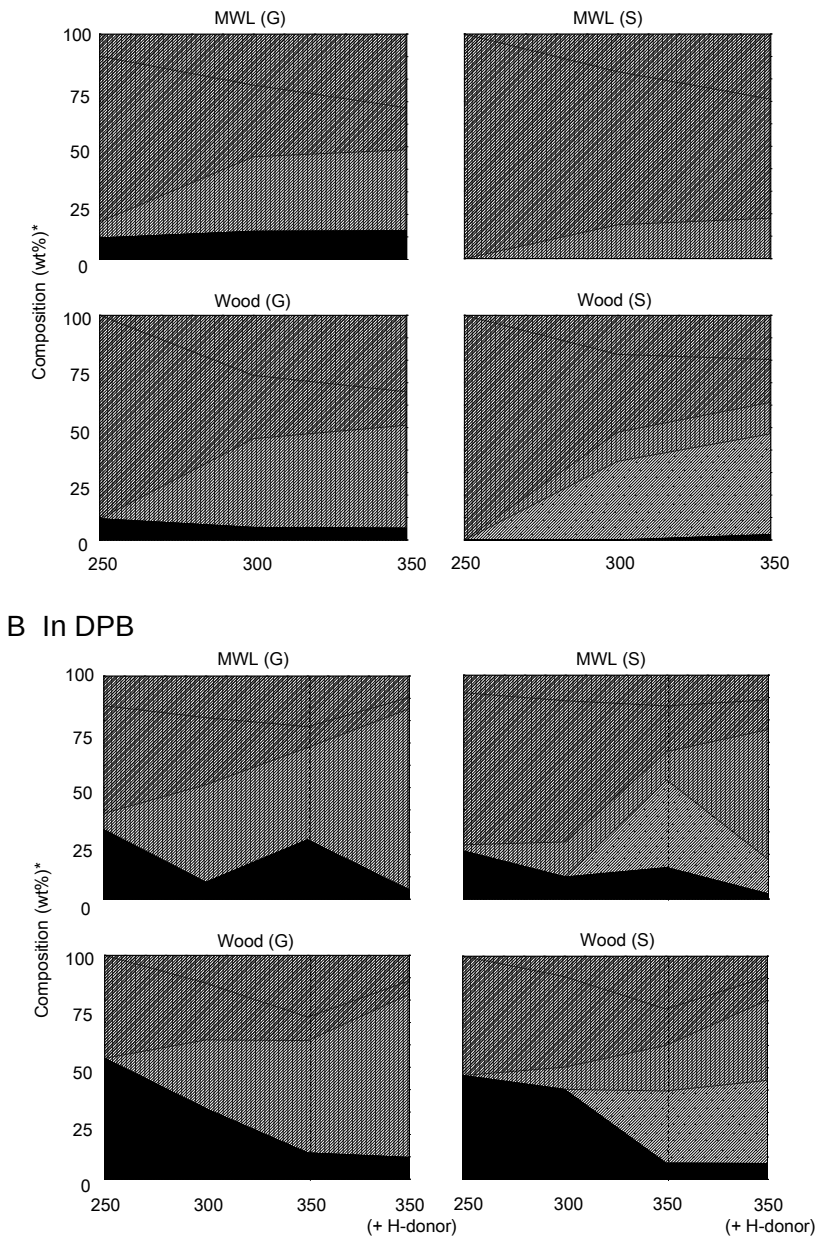


Fig.8 (single column)

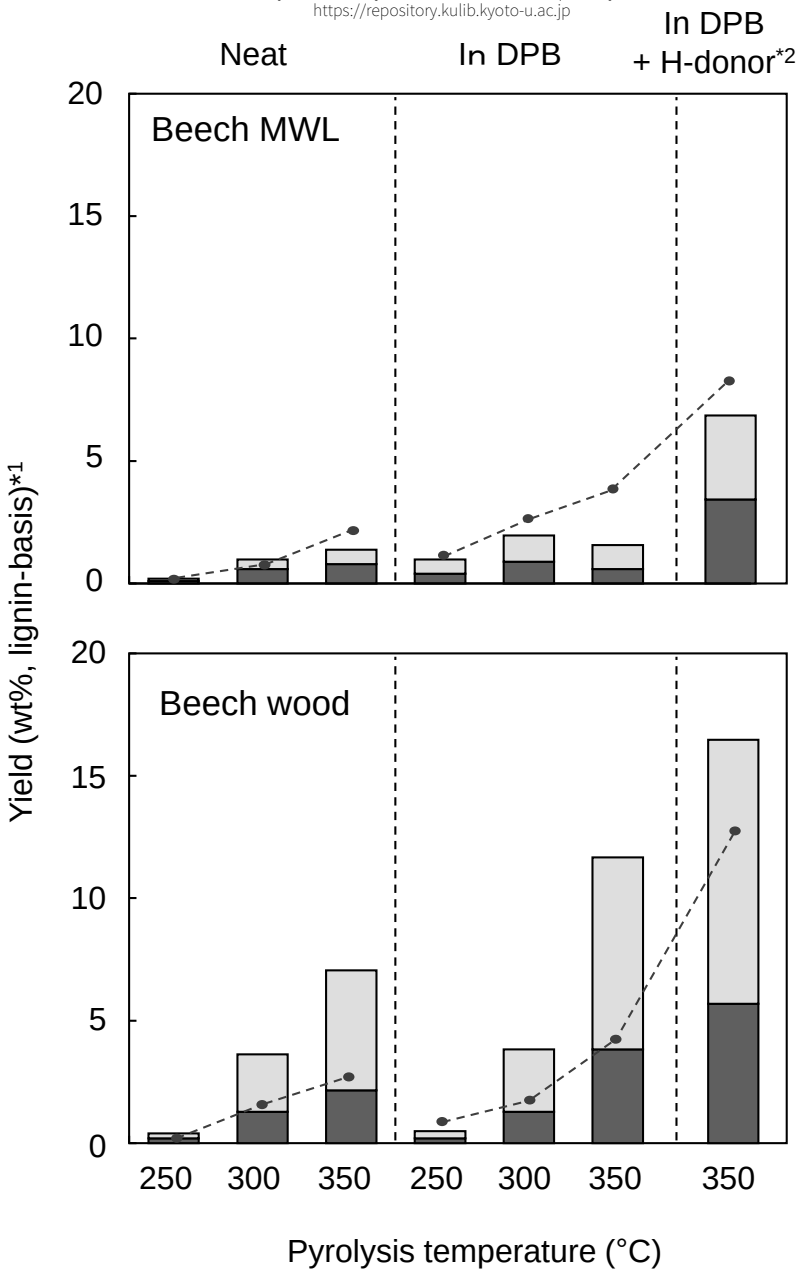


Fig.9 (single column)

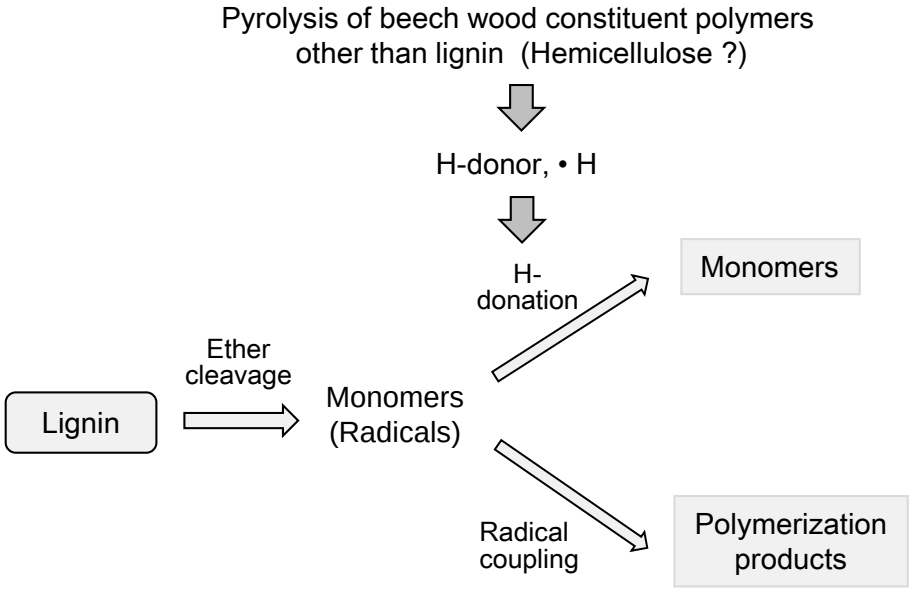


Fig.10 (single column or 1.5 column)